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# Synthesis And Characterization of the Al-Doped and Al–Mn Co-Doped ZnO Nanoparticles by Sol Gel Method

KEYWORDS: XRD, PL, Sol gel, emission, excitation

| K.Karunakaramoorthy | G.Suresh |
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| Department of Engineering Physics,Faculty of Engineering and Technology, Annamalai University,Chidambaram-608002. Tamilnadu, India | Department of Engineering Physics,Faculty of Engineering and Technology, Annamalai University,Chidambaram-608002. Tamilnadu, India |

**ABSTRACT** *In this work, the ZnO, Doped ZnO nanoparticles were synthesized by Sol Gel method using Zinc Acetate as a starting material and Aluminium acetate, Manganese acetate were used as a doping materials. The XRD analysis indicated that the synthesized nanoparticles have the hexagonal wurtzite ZnO structure. Further the samples were investigated by Scanning Electron Microscope (SEM), Energy dispersive X-ray analysis (EDAX), Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL). FT-IR spectra exhibited only absorption bands of the metal oxide groups. The PL -spectra revealed the emission peak at 403, 460nm by the excitation of 360 nm*

**Introduction:**
The binary metal oxides nano materials have attracted great attention because of their remarkable properties and potential applications in various nanodevices. The metal oxide reproduction was suitable for a wide range of applications. To make further development the physical and chemical properties, an interest in ternary complex oxides has become noticeable in recent times. Ternary nanomaterials have been attracting much attention for future science and technology.

Among them, Zinc aluminate spinel ($ZnAl_2O_4$) is one of the metal oxide semiconductors suitable for use in photoelectronic devices [1, 2]. ZnAlO is wide band gap semiconductor (Eg~3.8eV). The ZnO presents a great interest for the scientific Community due to its applications in different fields: electronics [3], opto-electronics [4], dielectrics [4], and sensing materials [4], as a photocatalyst [5] and as an antimicrobial agent [6]. Now a day, various routes have been used for the synthesis of Zinc aluminate nanomaterials, such as solid-state reaction [7], co-precipitation [8], hydrothermal [9.], spray pyrolysis [10], combustion [11] and sol–gel method [12]. The sol-gel technique offers composition, high purity, high quality, easy introduction of doping elements and a low-temperature method for synthesizing nanomaterials.

In this work, the effects of dopants on the microstructure and optical properties of ZnO and doped ZnO were investigated. The effects of doping on the structural and optical properties of zinc oxide nano particles were investigated by X-ray diffraction, SEM, EDAX, FTIR and photoluminescence.

**Experimental detail:**
**Materials:**
For synthesis of zinc oxide, Al doped Zinc Oxide and Al, Mn co-doped zinc Oxide nanocomposits the following materials were used. Zinc Acetate (1M) is starting material and Aluminium acetate (1M), Manganese acetate (1M) were used as a doping materials. The 2.methoxy ethanol was used as a solvent. Acidic acid add as gellating agent and ethylene glycol act as reaction medium. The ammonium hydroxide solution is added into the solution to adjust the pH at the suitable value.

**Preparation:**
In the preparation of Zinc Oxide sols, the following procedure was carried out; zinc acetate starting material was dissolved in 2 methoxy methanol solution. The acidic acids and ethylene glycol was added to the solution in 1:1 ratio. The mixed solution will keep under constant stirring at room temperature using magnetic stirrer. The ammonium hydroxide solution was added to the mixed solution with constant stirring until pH 10.3 was reached. The resultant solution was kept for gellation at 80 °C with constant stirring for approximately 5 hours from which the Zinc Oxide nanomaterials in the form of powder was obtained. The resultant powder was annealed at 900$^0$c. The Al doped Zinc Oxide and Al, Mn co-doped Zinc Oxide was carried out by the addition of Aluminium acetate, Manganese acetate with similar procedure. The final powder samples annealed at 900˚c temperature.

**Result and discussion:**
Fig. 1(a-c) shows the typical X-ray diffraction patterns for the ZnO, Al doped ZnO and Al, Mn co doped ZnO powder samples annealed at 900$^0$ c temperature. The observed diffraction peaks in the recorded XRD patterns correspond to those of the standard patterns of ZnO polycrystalline and correspond to hexagonal wurtzite structure (JCPDS No. 75-0576]. The peak intensities of prepared powder at 36.336˚ (2 theta) and that of standard data were the same. No diffraction peaks of Al, Mn or other impurities phases are detected in our samples, indicating that Al, Mn ions would uniformly substitute into the Zn sites or interstitial sites in ZnO lattice.

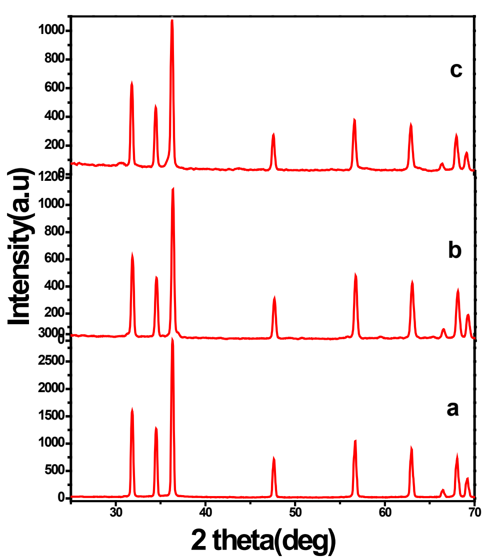


**Fig1 (a) XRD patterns of ZnO, (b) Al doped Zinc Oxide, (c) Al, Mn co-doped Zinc Oxide.**

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From fig 1(b-c), after the doping of Al and Al, Mn co-doped ZnO nano particles appeared in the polycrystalline structure. The average crystallite size of all the ZnO and doped Zinc Oxide nanomaterials was calculated using Scherrer formula [13]

$$d = \frac{0.9\lambda}{\beta cos\theta_B}$$

Where $\lambda$ is the x-ray wavelength of 1.54A °, $\theta_B$ is Bragg diffraction angle, and $\beta$ is the FWHM of $\theta_B$.

The calculated average crystallite sizes of pure ZnO, Al doped ZnO and Al, Mn co-doped ZnO annealed at 900'c is (90.76, 50.69, 68.50nm), respectively.

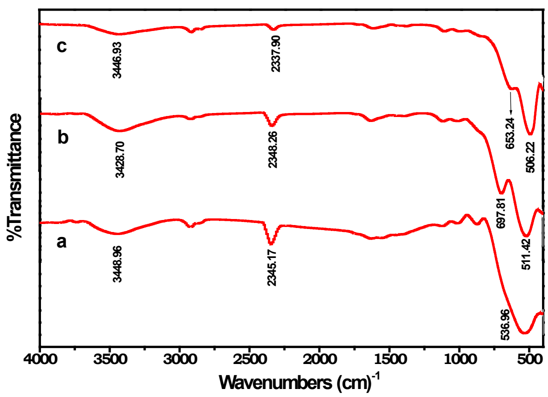


**Fig2 (a) FTIR spectra of ZnO, (b) Al doped Zinc Oxide, (c) Al, Mn co-doped Zinc Oxide,**

Using KBr pellets the Fourier transform infrared spectra of the pure and doped ZnO powders were recorded range of 4000 to 400 $cm^{-1}$ as shown in fig-2(a-c). The broad band at 3448, 3428, 3446 $cm^{-1}$ can be assigned to vibration mode of chemically bonded hydroxyl groups. The band at 1627 $cm^{-1}$ attributed to the deformation Vibration of water molecule. The absorption band at 2345, 2348, 2337 $cm^{-1}$ is due to the stretching vibration of $CO_2$. Below 700 $cm^{-1}$, a single strong peak around 536 $cm^{-1}$ was observed in fig 2(a). Fig. 2(b, c) exhibits two vibration bands between 500 to 900 $cm^{-1}$. According to Dhakand Pramanik [14], the spinels display stretching bands in the 500–900$cm^{-1}$ range, associated with the vibrations of metal–oxygen, aluminum–oxygen and metal–oxygen–aluminum [15-17]. So the doped samples show the two peaks around 500 to 900 $cm^{-1}$ for all the nanomaterials that is assigned to the formation of metal aluminates [18, 19]

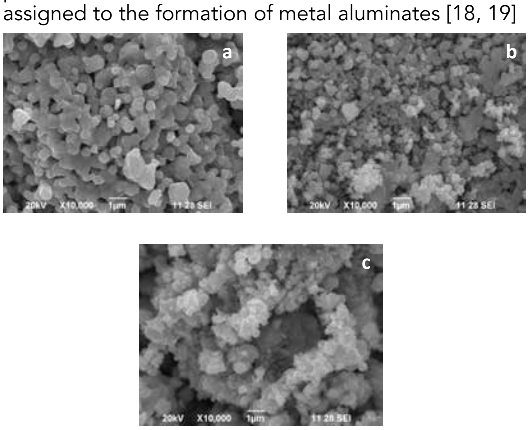


**Fig3 (a) SEM images of ZnO, (b) Al doped Zinc Oxide, (c) Al, Mn co-doped Zinc Oxide,**

The surface morphology of material in the form of granular structure with round morphology and little agglomeration were investigated with a scanning electron microscope. Fig.3 (a-c) shows SEM of ZnO, Al doped ZnO and Al, Mn co doped ZnO. It shows uniform distribution of pores with clusters of crystallites over the entire material. The Al-doping did not significantly change the appearance of the particles but Mn-doping alters the appearance of the particles.

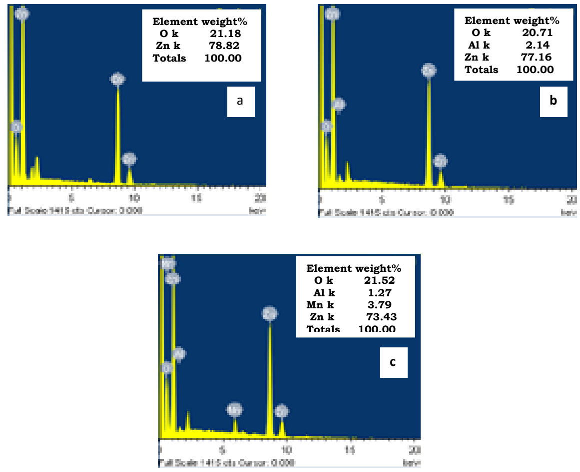


**Fig4 (a) EDAX images of ZnO, (b) Al doped Zinc Oxide, (c) Al, Mn co-doped Zinc Oxide,**

The elemental and weight ratio analysis of various doping elements in the samples obtained from fig 4(a-c). The Energy dispersive X-ray analysis shows the presence of Zn, Al, Mn and O. The hydrogen in hydroxyl phase cannot be detected.

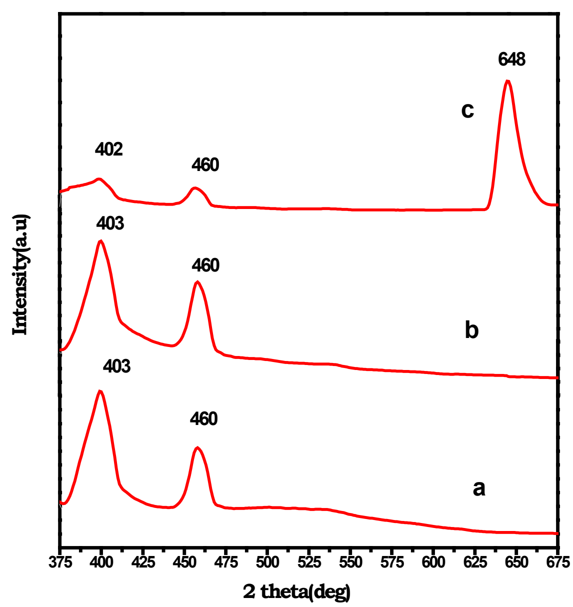


**Fig5 (a) PL spectra of ZnO, (b) Al doped Zinc Oxide, (c) Al, Mn co-doped Zinc Oxide,**

The photoluminescence spectra of ZnO, Al-doped ZnO and Al–Mn Co-doped ZnO nanoparticles under 360 nm excitation wavelength is shown in Fig5(a-c) respectively. The PL emission spectra of ZnO and Aluminium doped ZnO exhibit two emission bands with corresponding peak wavelengths of 403 nm and 460 under excitation of 360nm. A red photoluminescence was observed from Mn2+ doped ZnO nanocrystals whose peak is located at 648 nm. No red photoluminescence from ZnO and Al doped ZnO alone was observed.

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**Conclusion:**

The sintered precursors yielded nanocrystalline ZnO, Al doped ZnO and Al, Mn co doped ZnO were synthesized successfully by a sol–gel process. The structural, morphological and optical properties were examined. The prepared samples have hexagonal wurtzite structure when characterized by XRD and the evaluated average particle sizes are 124.72 nm, 48.51 nm and 80.69nm respectively. SEM images of the samples show the formation of granular structure and agglomeration. The Energy dispersive X-ray analysis shows the presence of Zn, Al, Mn and O. FT-IR revealed the presence of metal–oxygen, aluminum–oxygen and metal–oxygen–aluminum bands indicating the formation of ZnO, Al doped ZnO and Al, Mn co doped ZnO phase. The PL emission spectra of ZnO and Aluminium doped ZnO exhibit two emission bands with corresponding peak wavelengths of 403 nm and 460 nm under excitation of 360nm. A red photoluminescence was observed from Al, Mn co-doped ZnO nanoparticles whose peak is located at 648 nm.

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